The role of different soil management on the distribution of heavy metals in surface waters

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1. Abstract

The purpose of this work is to analyze the dissolved Cu, Zn, Mn, Fe and Al variations in surface waters at scale catchment during different soil management (NW Spain). The management types carried out in the catchment were: agricultural catchment with spreading of slurries using a conventional tank, agricultural catchment with intensive slurry application, reforested catchment without slurry application.

The results show that there is a great temporal variability for each metal and also among metals. The mean concentrations of studied metals were highest in the agricultural period. They all present the highest concentration peaks in the agricultural catchment phase with massive slurry application. This period especially affected the concentrations of dissolved copper and manganese, as well as those of zinc and to a lesser extent those of aluminum and iron. The effects of inadequate management in the application of slurries during the period of intense agricultural activity were reflected in the metal concentration of the waters of the catchment.

2. Introduction

The soil is a long-term sink for heavy metals. Although these elements have different mobility and bioavailability in soils, leaching losses and plant uptake are usually relatively small compared with the total quantities entering the soil from different sources. As a result, they slowly accumulate in topsoils, with long-term implications for agricultural soil quality and function. Heavy metal losses at the catchment scale depend largely on land-management practices and land use. Changing land use can affect the amount and quality of runoff during and following rainfall (Ren et al., 2002; Taboada et al., 2003; Soto et al., 2005). Certain agricultural practices may increase or decrease the mobility of some pollutants and in this way affect the water quality. When applied to agricultural land manures in amounts greater than can be utilized by crops and retained by the soil, manure constituents may be transported to surface water and groundwater through runoff and infiltration and contaminate the waters with microbial, antimicrobial agents, nitrates, salts, and metals (Adriano, 1986; Jones et al., 2002). Certain heavy metals may enter livestock diets from contaminants in mineral supplements. The majority of heavy metals consumed in feed are excreted, and will thus be present in the manure subsequently applied to land. Manures also contain some metals ingested with drinking water or added with bedding materials (e.g. straw). Depending on the manure management and storage system operated, manures (particularly slurries and dirty water) may contain metals from washing water (e.g. from dairy parlours) and veterinary products (Critchley, 1983; Menzi and Kessler, 1998; Nicholson et al. 1999). In addition, corrosion of the galvanised metal used to construct livestock housing and licking and biting of metal housing components are also a potential source of Zn in some manures. The discharge of untreated organic wastes in aquatic systems, results in hypoxia and anoxia in receiving water bodies, and increased concentrations of reduced chemical species, such as NH^{+4}, Fe^{+2} and Mn^{+2}. It is generally combined with high faecal contamination (Geldreich 1989) and is the most common and earliest form of water quality degradation (Meybeck et al. 1989; Kimstach et al. 1998).

Heavy metals, nutrients, and other chemical contaminants are transported in water bodies, dissolved or associated to sediment particles. It is known that the dissolved divalent ionic form of trace metals is toxic to the biota, while the adsorbed or particulate fraction is considered biologically unavailable. Some heavy metals such as zinc and copper are important in small quantities for biological processes in aquatic plants and animals and occur naturally in many river systems. However, when they are discharged in large quantities from sewage or agricultural runoff, they can be extremely harmful. Heavy metals can also accumulate in sediments; thus, they can pose a significant and persistent threat to ecosystem health. As a consequence, there has been increasing awareness of the importance of determining the heavy-metal contents in streams for the purpose of assessing water quality and geochemical properties (de Vries et al. 2002).

An increase in dissolved and sediment associated heavy-metal contents in aquatic systems due to anthropogenic activities can result in a significant threat to water quality (Holgate 1979; Meybeck and Helmer 1989; de Vries et al. 2002).

Increased attention has been given in the study region to measurement of suspended sediment properties. However, heavy-metal concentration data at the small catchment scale are rather scarce. The purpose of this work is to analyze the dissolved Cu, Zn, Mn, Fe and Al variations in surface waters at scale catchment during different soil use and management in a small catchment located in the northwest of Spain.

2. Methods

The study was carried out in the "Abelar" experimental catchment (area 10.7 ha), located in the A Coruña Province (NW Spain), 8°21'15" N, 43°9'10" W. The geological substrate is schist of the "Ordenes Complex". Soil texture is basically silty loam (sand 30%, silt 50%, clay 20%) throughout the watershed. Mean organic matter content is 9.5%, and pH in water 5.2. The study area receives an annual mean rainfall of approximately 1400 mm. Its mean slope is 6.9%. For many years, most of this catchment was used as agricultural land. This site was impacted mainly by cattle grazing and bovine and porcine slurries. Agricultural activities and manure deposition ceased toward the end of July 1998, and since then most of the catchment was planted with *Eucalyptus globulus*. The use and management types carried out in the catchment were: agricultural catchment (mainly pasture and forage maize) with spreading of slurries using a conventional tank, agricultural catchment (pasture and land fallow) with intensive slurry application, reforested catchment almost entirely occupied by *E. globulus* and without slurry application.

Water samples were collected from the catchment outlet-point between January 1997 and July 2002. For analysis of heavy metals, the water was collected in acid-cleaned polyethylene terephtalate bottles. Samples were filtered using 0.45 μm filters. The filtrate was acidified to pH 2 using Merck Suprapur HNO_3. Heavy metals were analysed by ICP-MS (VG-PlasmaQuad-PQ 2).

3. Results

Figure 1 shows a comparison between metal levels in agricultural and forestal use. Mean metal concentrations were very variables between the two periods, the highest values always produced in the agricultural period. So, Cu was about 7 times greater in the latter, that of Mn 5 times greater, and those of Zn, Fe and Al twice greater. On the other hand, the minimum and maximum values were greater in the agricultural than in the forestal. As can be seen, the agricultural activity, mainly the fertilizer with slurry, tends to increase the concentration of these elements in surface waters. However, the mean content of metals in forestal period is much higher than the global mean proposed by Meybeck and Helmer (1989) for not polluted rivers. In addition, the values of Abelar catchment were even higher than those obtained in agroforestal catchment near the study area (Diéguez, 2005; Rodríguez et al., 2005).

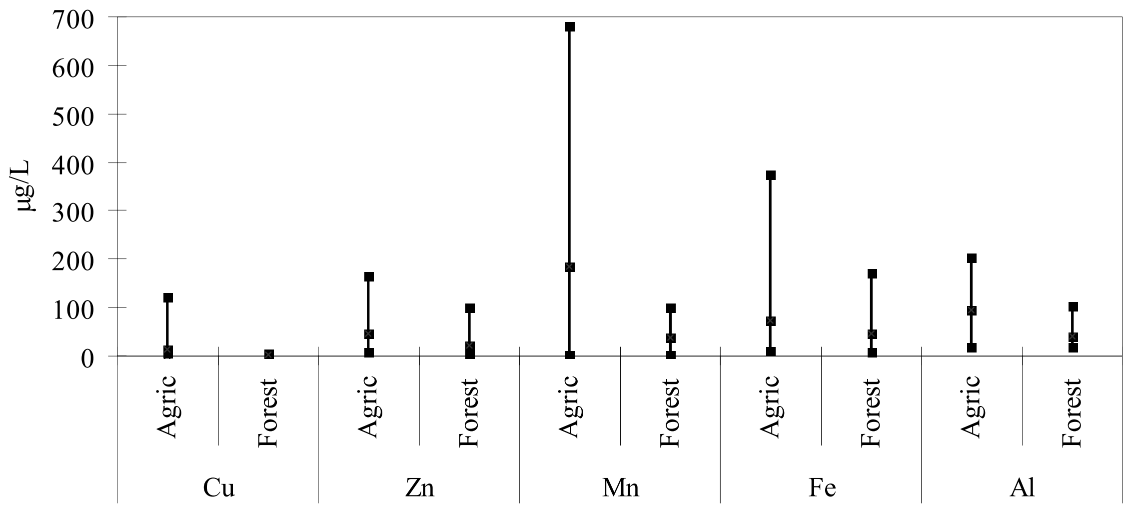

Figure 1 Comparison of mean and range metal concentrations in agricultural and forestal use

There is great temporal variability for each metal and also between metals. All metals present the highest concentration peaks in the period with intensive slurry application. In the remaining period of study the distribution of concentrations was quite different for each metal, although all showed a more or less marked tendency toward a reduction in concentration when going from the agricultural to the forestal period. Figure 2 shows an example for Cu and Zn.

The transport of metals from soils to surface waters is a complex process involving natural and anthropogenic factors. Among the anthropogenic factors, the slurries seem to have contributed notably toward the increase in the concentration of dissolved metals in the second phase of the agricultural period although they seemed to have affected each element in a different way. The effect of the slurries could be due to the contribution of metals proceeding from these residues as well as to the solubilization of soil metals, as indicated others authors (Japenga et al., 1992, Nicholson et al. 1999).

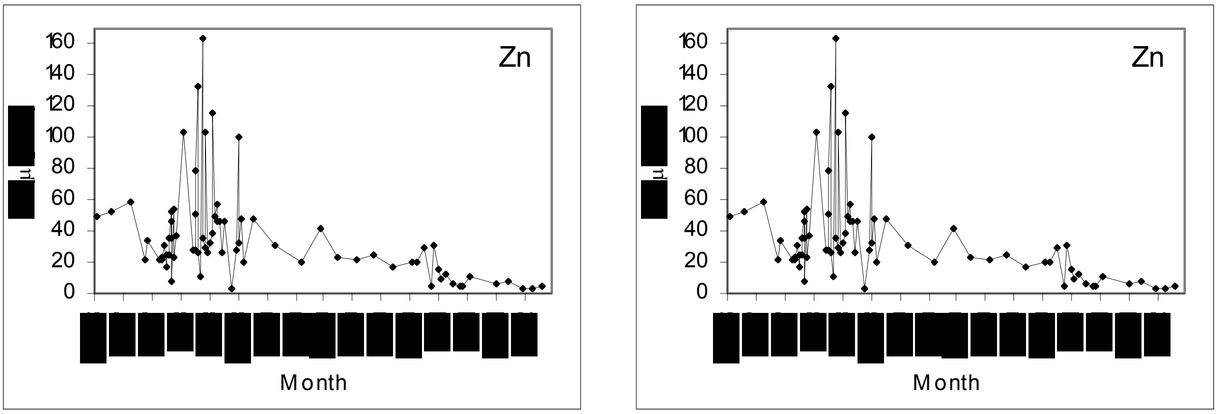

Figure 2 Evolution of dissolved of Cu and Zn concentrations in the water at the catchment outlet

4. Conclusions

Temporal variations in heavy metals at the catchment outlet suggest that dissolved metal concentrations are controlled by the land use and management practices. Important differences in metal contents were found between agricultural and forestal period, the highest metal losses occurred during first one. The slurries seem to have contributed notably toward the increase in the concentration of dissolved metals in the surface water of the catchment, affecting the water quality.

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